

Functionalization of the Si(1 1 1) 7 × 7 substrate with coronene molecules using simple molecular source

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The present paper aims at describing a source designed and constructed to generate an organic molecular beam under ultrahigh vacuum conditions. The presented construction solution of the evaporation source allows for independent deposition of three different kinds of molecules. The probability of molecules fragmentation is minimized by using a thermocouple being in contact with a molecular crucible, which enables precise temperature control. In addition, cleanness and molecular beam density are monitored using a quadrupole mass spectrometer and quartz microbalance, respectively. The operational parameters of the molecular source are optimized and deposition rates are measured for the coronene molecule in the sublimation temperature range between 430 K and 460 K. The analysis of scanning tunneling microscope images of the Si(1 1 1) 7 × 7 substrate covered with the sub-monolayer of coronene molecules and comparison with previously published data has been used for verification of the molecular source operation.

Keywords: *molecular source; coronene; Si(1 1 1); scanning tunneling microscopy (STM)*

1. Introduction

The Si-based technology dominates in the application of semiconductor devices. Further development of the semiconductor technology needs the application of different materials and systems to obtain faster or more economical components incorporated into the existing silicon (Si) technology [1, 2]. For this reason, different semiconductor systems are being intensively investigated to solve specific problems, e.g. formation of the metallic contacts [3, 4], monoatomic passivation layers [5–8] or thin insulating layers [9, 10]. On the other hand, local surface defects or adsorbed molecules are considered for the controlled nanostructures growth [11–13]. The aromatic molecules deposited on the substrates are often used to grow graphene flakes and layers on metallic [14, 15] and semiconductor substrates [16, 17].

The ability to control the process of molecules deposition is a key issue for the surface functionalization and graphene layer growth [13, 18, 19]. Maintaining relevant properties of the substrate is

possible by using ultrahigh vacuum (UHV) conditions which are necessary in generation of a pure molecular beam. The organic molecules in the liquid phase could be evaporated using a simple evaporator connected through a needle-type valve to the processing chamber [18]. In order to deposit the molecules in the solid state via the thermal evaporation, an evaporator with ceramic pipes [20, 21] or a heated quartz glass barrel [22, 23] is frequently used.

This paper presents the constructed molecular source designed to generate the molecular beam under UHV conditions. The proposed constructional solution allows independent deposition of three different kinds of molecules, excluding cross-contamination. The probability of molecules fragmentation is minimized by using precise temperature control with a thermocouple being in contact with the crucible containing molecules. In addition, cleanness and molecular beam density are monitored using a quadrupole mass spectrometer (QMS) and quartz microbalance, respectively. The operational parameters of the molecular source are optimized and discussed in detail. The functionalization of the reconstructed Si(1 1 1) 7 × 7 surface

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with the sub-monolayer of coronene molecules is characterized by means of scanning tunneling microscopy (STM). The analysis confirmed the proper molecular source operation and developed our fundamental understanding of the mechanism of isolated organic molecule interaction with the reconstructed Si surface.

2. Experimental

2.1. Experimental setup

The investigations have been carried out under UHV conditions with a base pressure at the level of 1×10^{-8} Pa. The STM measurements were performed using a commercial microscope operating at room temperature (RT). The part of the UHV system was intended to sample preparation and it consisted of standard sample preparation devices (a sample heating stage, an Ar^+ sputtering ion gun, gas lines and a quartz crystal microbalance). The constructed homemade molecular source (described further, including calibration) was also connected there. The thickness of the deposited molecular layers was measured by the quartz crystal microbalance. Total and partial pressures inside the preparation chamber were controlled by the cold cathode gauge and QMS with a continuous secondary electron multiplier (C-SEM), respectively.

The molecular beam was used to Si(1 1 1) 7 × 7 substrate modification to validate the molecular source operation. The commercially available p-doped Si sample was mounted on the standard molybdenum sample holder. The sample preparation procedure included thermal cleaning and ion bombardment. Initial cleaning started with degassing the sample for 2 hours at a temperature of ~ 870 K by direct heating method. At the next step, the cleaning process started with an ion bombardment by Ar^+ ions with the energy of 0.7 keV for 30 min under Ar partial pressure of 5×10^{-4} Pa. Then the substrate was flashed 8 times at ~ 1400 K for 10 s to induce surface reconstruction [12].

STM images were obtained for both as-prepared and modified with coronene molecules samples. The bias voltage was varied in the range from +3 V to -2 V using the tunneling current

range of 500 pA down to 100 pA. STM tungsten tips were electrochemically etched and cleaned by sputtering with Ar^+ ions before use. The STM data processing was carried out by using the Gwyddion software [24].

2.2. Evaporator design

The UHV molecular source has to meet the following assumptions: the generation of a pure molecular beam, the beam intensity control and possibility of deposition of three different kinds of molecules at the same time (the system of three independent crucibles). Beam density and molecules fragmentation should be monitored by precise control of the crucible temperature using thermocouples. The design of the molecular source is shown in Fig. 1.

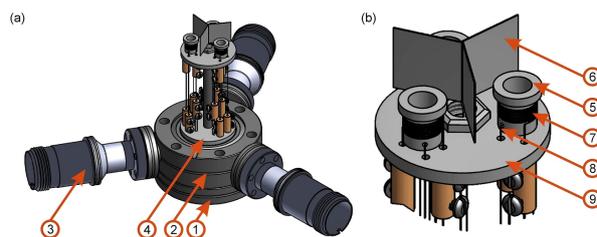


Fig. 1. Scheme of the molecular source used in this investigation: (a) overall view; (b) zoom of the crucibles mounting system; 1 – blanked DN 40 CF flange with supporting rod welded in; 2 – spacer flange DN 40 CF; 3 – electrical feedthrough; 4. bottom AlN ceramic spacer; 5 – aluminum nitride crucible; 6 – collimation shutter; 7 – tungsten heater; 8 – K-type thermocouple; 9 – top AlN ceramic spacer.

The molecular source is mounted on the preparation chamber using a standard ConFlat (CF) flange system. The supporting element of the source consists of the blanked DN 40 CF flange 1 with a rod welded to the inner part of the flange. The spacer flange 2 with three DN 16 CF ports connects the base flange with the preparation chamber. The ports of the spacer flange are connected with 4-pins electrical feedthroughs 3 (alumel pins, maximum current 10 A). The pins are bent to pass through the bottom AlN ceramic spacer 4. The top part of the source consists of three cylinder-shaped

aluminum nitride crucibles 5 with capacities of $\sim 0.2 \text{ cm}^3$. The crucibles are separated with the tantalum collimation shutter 6 which protects against contamination and influence of heat transfer between the crucibles. The tungsten heaters 7 are coiled on the threaded crucibles. A hole of 1 mm diameter is located on the crucible base which is made to fix the K-type thermocouple 8. This kind of thermocouple permits a precise control of the crucible temperature to 1523 K [25] with the accuracy of 0.1 K. The thermocouples and heaters connections pass through the holes in the top of AlN ceramic spacer 9. The AlN ceramic spacers stabilize the system and separate the thermocouples and heaters wires. Between the spacers, the electrical feedthroughs pins are connected with the heaters and thermocouples by standard UHV compatible Be/Cu barrel connectors.

3. Results and discussion

3.1. Source calibration

Coronene, which is commercially available, is an organic molecule consisting of C_{24} and H_{12} and is an example of polycyclic aromatic hydrocarbon (PAH) [26]. The optimization of the molecular source operational parameters was obtained for the crucible containing about 0.5 g coronene powder.

The experimental results of the source optimization are presented in Fig. 2. One should note that the crucible was initially degassed at the temperature of 400 K to enhance source contamination desorption. The dependences of coronene layer thickness versus time for different crucible temperatures are shown in Fig. 2a. The layer thickness was monitored by means of quartz crystal microbalance with the microbalance detector located at the sample position. The presented dependences were recorded after molecular beam stabilization for at least 3 min. The observed relations are strongly linear (R-square factors are higher than 0.99) and they allow precise determination of the deposition rates. The dependence of the deposition rate versus crucible temperature is shown in Fig. 2b. The relation between the deposition rate and temperature is exponential according to Arrhenius relation, i.e.:

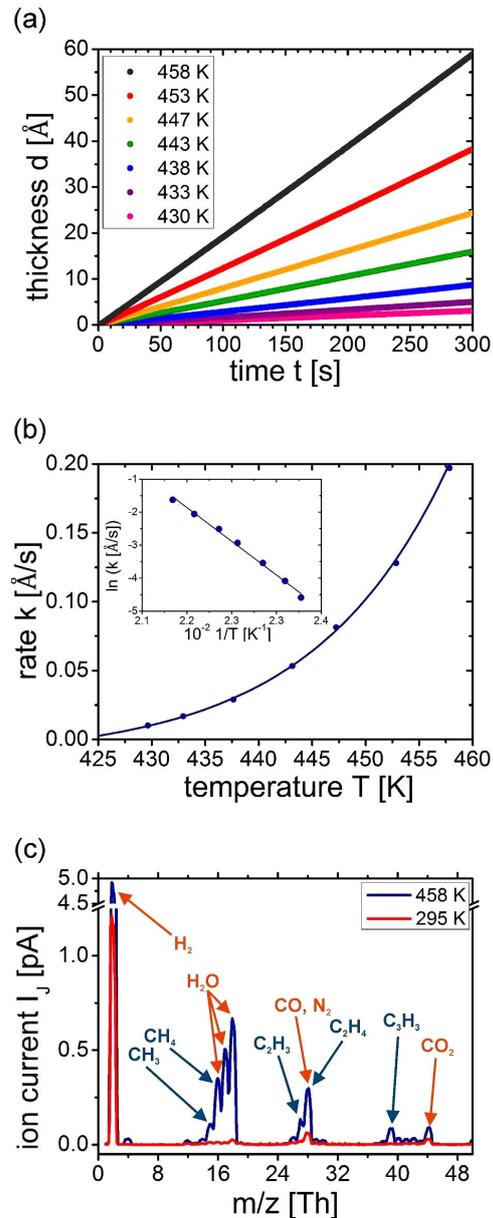


Fig. 2. (a) experimental dependence of coronene layer thickness versus time for different crucible temperatures; (b) experimental values of coronene deposition rates k for different crucible temperatures; (c) mass spectra of residual gases: before (red solid line) and immediately after (blue solid line) the deposition process.

$$k = k_0 \cdot \exp(-E_a/RT) \quad (1)$$

where: k is a deposition rate [Å/s], k_0 is a constant pre-factor [Å/s], T is the crucible temperature in K and R is a universal gas constant. E_a is considered

as a molecular activation (sublimation) energy. The activation energy value estimated from the linear regression of: $\ln k = \ln k_0 - \frac{E_a}{RT}$ (inset in Fig. 2b) is equal to 170 ± 6 kJ/mol.

The impact of source operation on vacuum conditions and quality was analyzed. The total pressure has not changed significantly during the deposition process and has not exceeded 10^{-8} Pa level. More detailed information could be obtained from partial pressure analysis by QMS. Before the deposition process, signals of H_2 , CO, CO_2 or N with the intensities typical of UHV conditions were observed (red solid line in Fig. 2c). In contrast to the above mentioned example, the QMS spectrum, corresponding to the 458 K crucible temperature, is presented in Fig. 2c (blue solid line). The peaks corresponding to the gases observed before are still present but with higher intensities (about 5 times). There are also additional peaks of water molecules (18 kg/C, 17 kg/C and 16 kg/C) and hydrocarbon groups (15 kg/C, 16 kg/C, 28 kg/C and 39 kg/C, attributed to the CH_3 , CH_4 , C_2H_4 and C_3H_3 , respectively). The appearance of the water molecules could be explained as a result of the contaminants desorption mainly out of the evaporation source components. The hydrocarbon groups signals serve as an evidence of coronene molecules sublimation and their fragmentation in the QMS' ion source. The optimization of the source operational parameters allows us to control the coverage as a function of both time and temperature parameters.

3.2. STM investigation

Fig. 3 presents an overview of the prepared Si(1 1 1) 7 × 7 substrate. The large field view STM image of the surface shows atomically flat terraces, which are monoatomic in height (~ 3 Å) (Fig. 3a). Fig. 3b and Fig. 3c show the characteristic atomic structure of the clean Si(1 1 1) 7 × 7 surface (imaged in both unoccupied and occupied states, respectively) with the elementary surface rhombohedral unit cell with diagonals of about 4.7 nm and 2.7 nm. The recorded surface structure is in agreement with the studies done previously [27, 28].

Then, the prepared substrate was modified by the deposition of the coronene molecules using

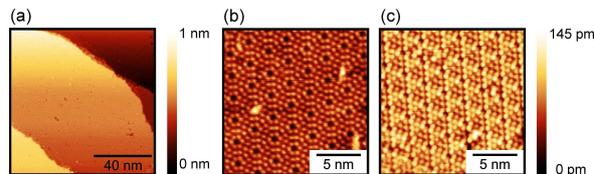


Fig. 3. Constant current STM images of atomic structure of the reconstructed Si(1 1 1) surface; (a) large scale overview of the atomically flat terraces ($U = 2$ V, $I_t = 100$ pA); (b) reconstructed surface obtained with positive bias voltage ($U = 2$ V, $I_t = 500$ pA); (c) reconstructed surface obtained with negative bias voltage applied to the sample ($U = -2$ V, $I_t = 500$ pA).

the homemade molecular source described in this paper. After the molecular beam stabilization (verified by quartz crystal microbalance), the sample was placed perpendicularly in the site of maximum molecule flux for 30 s. During the exposure, the crucible temperature was set at 430 K, pressure was equal to 8×10^{-8} Pa. The results of the coronene deposition are presented in Fig. 4. The evaluated coverage is about 0.1 ML (1 ML corresponds to a single coronene molecule layer covering the whole surface of the substrate).

The general overview of the obtained coronene sub-monolayer with the marked characteristic features attributed to the molecules is presented in Fig. 4a. The blue rhombus indicates an elementary surface unit cell of Si(1 1 1) 7 × 7 substrate reconstruction. A close look at this image shows that coronene molecules (triangular in shape and marked with a blue circle in Fig. 4a) prefer the position inside the half of the surface unit cell, in the same direction with respect to the surface directions and are stretched out between three corner holes. This tendency results from the differences in electronic properties between faulted and unfaulted halves of the elementary surface unit of Si(1 1 1) 7 × 7, as a result of stacking fault configuration [28, 29]. The molecules are bonded with the surface by central adatoms of substrate unit cell and the most stable adsorption site is observed on the unfaulted half of the reconstructed Si(1 1 1) unit cell (dark blue circle in Fig. 4a) [30]. Despite these strong bindings, two kinds of molecules

displacement in RT have been noticed. The bright horizontal lines observed in Fig. 4a are consistent with fast scan direction in STM images and result from molecules rearrangement on the surface to find the most energetically favorable adsorption site. A different migration type of the molecules is marked with light blue circles in the same figure. The arrow signifies the direction of the displacement. Interaction between the tip and a molecule causes the transition of the molecule between energetically equal sites. It should be noted that between the molecules, the not-disturbed, still reconstructed Si(1 1 1) is visible and molecules desorption has not changed the substrate.

The detailed analysis of STM images obtained for various positive bias voltages confirms stable adsorption sites of the molecules (Fig. 4b, Fig. 4c and Fig. 4d). The images obtained at positive bias voltages in the range of 1.75 V to 3 V present the lowest unoccupied molecular orbitals (LUMO) of the molecules adsorbed in the unfaulted half of the unit cell [30]. The features from the molecules covalently bonded to the substrate disappear for the bias voltages range of 1.75 V to 1.25 V. In addition, the apparent vacancies have occurred in positions of the adsorption molecules sites in the Si(1 1 1) 7×7 structure for STM imaging with positive voltages below 1 V. The difference is strongly evidenced when Fig. 3b and Fig. 4d are compared. The STM occupied-state images (Fig. 4e, Fig. 4f and Fig. 4g), in contrast to STM empty-state, show the weakly bonded molecules only (adsorbed out of the preferred-unfaulted half-position in Si(1 1 1) 7×7 substrate) [30].

Fig. 5 presents the stable adsorption sites of coronene molecules on the Si(1 1 1) 7×7 substrate unit cell obtained at +3 V and +1 V bias voltages. The confirmation of changes in electronic properties is clearly visible when comparing 3D visualizations. A distinctly visible protrusion on the surface measured at positive bias voltage is caused by the stable adsorbed molecule. As a result of charge transfer between the molecule and substrate atoms, a signal from dangling bonds of central adatoms becomes visible as filled states. On the contrary, in 3D visualization in the STM image obtained

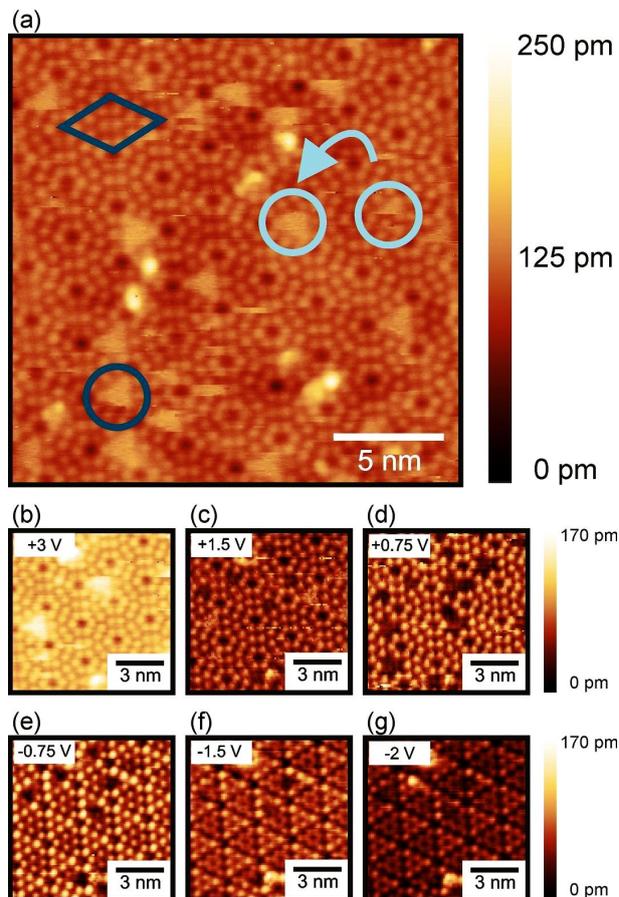


Fig. 4. Constant current STM images of the atomic structure after deposition of 0.2 ML coverage of coronene deposited on the reconstructed Si(1 1 1) 7×7 surface; (a) atomic resolution on the larger area view ($U = 3$ V, $I_t = 100$ pA); single 7×7 surface unit cell is indicated with a blue rhombus, an individual coronene molecule is marked with a blue circle and two light blue circles with an arrow indicating the single molecule surface diffusion induced by the scanning STM tip. The same area STM images: (b), (c) (d) unoccupied states and (e), (f) and (g) occupied states ($I_t = 100$ pA). Bias voltage values are given in the figures.

at the bias voltage of +1 V, it looks like concavity in site of the adsorbed molecule. All the described experimental observations are consistent with the previous report by Martinez-Bianco *et al.* [30], obtained after the deposition of coronene molecules using commercial Knudsen cell at a higher temperature (390 K).

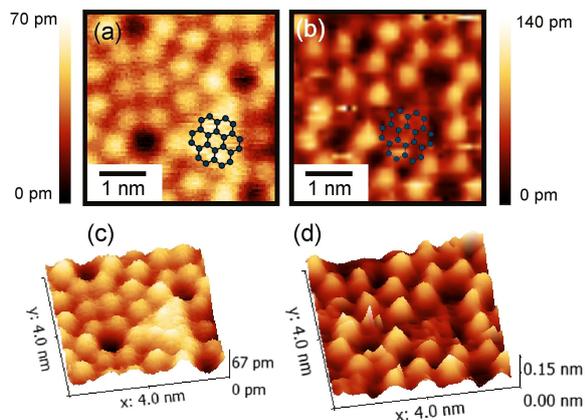


Fig. 5. STM images of a single substrate unit cell with adsorbed coronene molecule: (a) and (b) the top view of 5 nm × 5 nm area with a single molecule imaged at 3 V and +1 V biases, respectively, (c) and (d) 3D visualization of the images (a) and (b) ($I_t = 100$ pA).

4. Conclusions

The presented molecular source fulfils all the requirements necessary to evaporate gentle organic molecules without their fragmentation. It is fully UHV compatible and permits a controlled deposition of different kinds of molecules. The quartz crystal microbalance investigations enabled determining the molecular beam density and precise control of the coverage. Molecular flux purity was verified by the analysis of partial pressure of residual gases and finally by means of STM images of the coronene molecules adsorbed on the reconstructed Si(1 1 1) 7 × 7 substrate. The obtained results confirm the usefulness of the presented solution for controlled functionalization of substrates under UHV condition by organic molecules deposition and for characterization of interactions between molecules and a semiconductor substrate. The source construction consists of commonly available components and handmade elements. The system of the source is simple and it may be easily modified and extended to adapt it to other experimental setups.

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